

(11) (A) No. 1,117,685

(45) ISSUED 820202

(52) CLASS 400-72
C.R. CL. 204-91.32

(51) INT. CL. ³A61K 6/08, C08L 63/10

(19) (CA) **CANADIAN PATENT** (12)

(54) ONE PASTE POLYMERIC DENTAL RESTORATIVE
COMPOSITION

(72) Madhavan, Narayanan;
Freeman, Frank H.;
Singal, Rajendar,
U.S.A.

(73) Granted to Sybron Corporation
U.S.A.

(21) APPLICATION No. 288,773

(22) FILED 771014

(30) PRIORITY DATE U.S.A. (742,023) 761115

No. OF CLAIMS 20 - NO DRAWING

288773

ABSTRACT OF THE DISCLOSURE

FEB 2 1982

1117685

A long shelf life one phase photocurable dental composition is described. The polymerization is effected by a unique combination of an alpha diketone initiator and a tertiary amine accelerator. The composition is activated by actinic radiation.

B

DESCRIPTION OF THE INVENTION

This invention relates in general to photo polymerizable compositions and more specifically to those used in the dental field.

Photo polymerizable compositions known for use in the dental field, generally contain thermosetting acrylic esters of bisphenolic compounds, an acrylic monomer diluent, and a combination of photo polymerization initiator and accelerator. As a rule compositions of this nature are two part systems. U.S. 3,709,866 describes one such system where one component containing the initiator is kept separate from the rest of the composition and the two components are mixed by the dentist in a definite proportion just prior to using. This procedure is necessary to maintain a certain shelf life for these dental materials. Homogeneity in such a mix is almost impossible when a drop of initiator is mixed with an almost solid like composite. Failure to produce a homogenous mix may create irregularities within the restoration. In U.S. 3,759,807 Osborn and Trecker use a combination of an organic carbonyl compound and an amine, and more particularly the combination of benzophenone and a tertiary amine as the initiator and accelerator respectively. Though these compositions were polymerizable they could not be used as filling material for dental cavities because of their slow curing. Dental composite systems containing a derivative of diglycidyl ether of bisphenol A, an acrylic binder and a filler have been crosslinked with benzoyl peroxide or other suitable catalyst by Lee and Swartz in U.S. 3,539,533. They were found to have a compression strength of only 26000 psi (col. 5, line 64). Further, the presently available dental composite materials



are characterized by systems of two phases, i.e., paste-paste, paste-liquid, liquid-liquid or powder-liquid. The two phases are brought together according to certain proportions and mixed. The property of the final product depends upon how well and how fast one performs the mixing. In mixing the two phases, the air is incorporated into the compound which acts as polymerization inhibitor and produces mechanical flaws in the restorative material and is also slow curing. Further, the non-uniformity in mixing may lower the quality of the fillings. This deficiency is completely eliminated by the present invention.

Thus, it is an object of this invention to provide a uniform one paste dental filling compound having a long shelf life which does not require hand mixing or activating by the dentist prior to its use.

It is also an object of this invention to provide a dental restorative material having high compression strength.

It is another object of this invention to provide a novel initiator and accelerator composition for photopolymerizing the acrylic esters.

It is yet another object of this invention to provide a dental compound having a fast cure.

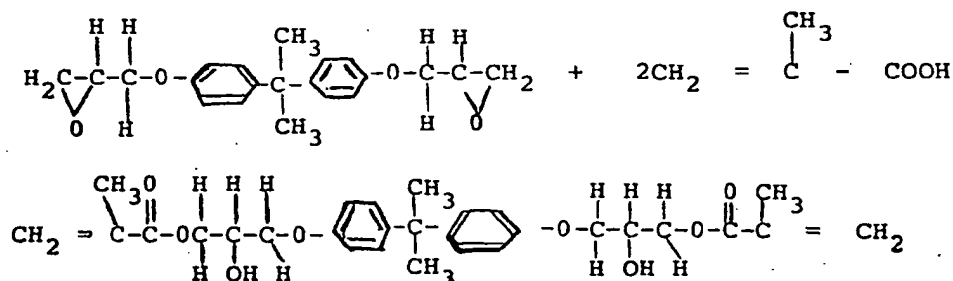
It is a further object of this invention to provide a system with a greater depth of cure especially in highly filled and pigmented dental composites.

It is also an object of this invention to provide an x-ray opaque dental material cured by the application of actinic radiation.

It is yet a further object of this invention to provide a single component dental composition for use as pit and fissure sealant, bonding agent, cavity liner and a restoration glaze.

The foregoing objects and others are accomplished in accordance with this invention by providing a composition containing a derivative of diglycidyl ether of bisphenol-A, an acrylic diluent, filler or a combination of fillers and a combination of an initiator -accelerator, comprising of alpha diketone and a tertiary amine respectively.

The advantages of this method will become apparent upon consideration of the following disclosure of the invention. Photopolymerizable compositions have been increasingly used in the recent years as restorative materials for filling dental cavities. Such compounds typically comprise a monomer resin containing unsaturated sites which are capable of undergoing polymerization, a diluent monomer to control the viscosity of the resin, a filler or a combination of fillers, an initiator which produces free radicals on exposure to actinic radiation, which then react with the double bond of the monomer to initiate polymerization and an accelerator which increases the speed of photo reaction of the composition. The resin used in the preparation of this single paste may be derived from the reaction of diglycidyl ether of bisphenol A, with methacrylic acid or acrylic acid:



This glycidyl methacrylate derivative of bisphenol-A is known as bisphenol A- bis(3-methacrylato-2-hydroxypropyl) ether. The resin serves as a binder for the photopolymerization dental composition, and is hereinafter referred to as Bis-GMA. Modification of this resin can also be used.

The diluent monomer used may be selected from alkyl methacrylates, alkylene dimethacrylates, trimethacrylates, alkyl acrylates, alkylene diacrylates, and triacrylates. Some of the suitable monomers are represented by:

10

Methylmethacrylate
Ethylmethacrylate;
Butylmethacrylate
n-propylmethacrylate
Isopropyl methacrylate
1,3-butylenedimethacrylate
Ethyleneglycoldimethacrylate
Triethyleneglycoldimethacrylate
1,6-hexaneglycoldiacrylate
Tetraethyleneglycoldiacrylate
Tetramethyleneglycoldimethacrylate, etc.

One or more of these monomers can be used. The diluent monomers copolymerize with Bis-GMA resin on exposure to actinic radiation light in the presence of photoinitiator and accelerator. The accelerator increases the speed of the reaction.

20

Another component present in the composite is a polymerization inhibitor which prevents the premature polymerization of the Bis-GMA resin and diluent monomer and is present only in small quantities. The suitable polymerization inhibitors are hydroquinone (HQ), methyl ether of hydroquinone (MEHQ), butylated hydroxytoluene (BHT), and triphenylstyrene.

Photo initiators generally are photosensitive carbonyl compositions. The initiators used in this invention are alpha diketones and their derivatives having the following general formula:

R-COCO-R'

Where R and R' can be same or different aliphatic or aromatic groups and their derivatives. Some of the examples are:

$\text{CH}_3\text{COCOCH}_3$	Biacetyl
$\text{CH}_3\text{COCOCH}_2\text{CH}_3$	2,3-pentanedione
$\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5$	Benzil
$\text{CH}_3\text{OC}_6\text{H}_4\text{COCOC}_6\text{H}_4\text{OCH}_3$	4,4'-dimethoxybenzil
$(\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5)_2\text{O}$	4,4'-oxydibenzil

These photo initiators are slightly yellow in color. Since they are present in small quantities, the final polymerized product is almost colorless.

Photo accelerators are chemical compounds which in the presence of initiators accelerate the photoreaction. The accelerators help polymerization penetrate a restoration placed into deep cavity preparation. The accelerators are amines (primary, secondary and tertiary) and diamines. Some examples are dimethylparatoluidine, N,N'-dimethylbenzylamine, N-methyl-dibutylamine, triethylamine, trihexylamine, etc. Examples of diamine, N,N,N',N'-Tetra ethyl ethylenediamine and N,N,N',N'-tetramethyl 1,6-hexanediamine.

In the absence of the previously mentioned photo initiators, these amines do not function to induce photopolymerization. Even though all amines in combination with the previously mentioned photoinitiators accelerate to some extent, the tertiary amines (eg. triethylamine, trihexyl amine etc) are found to be the best for causing polymerization deep into the composite mass. Amines with aromatic groups are not desirable as they impart a slight color on prolonged exposure to light.

When benzophenone and amine combinations, known in the prior art, are used in Bis-GMA system they either do not cause

polymerization or are slow curing. We have found that the unique combination of an alpha diketone as the photoinitiator with an amine as the polymerization accelerator and using actinic radiation as activator, produces a filling having a high crushing strength.

The photopolymerizable dental restorative product may have up to 85% refractory filler. At least 25% of said filler is barium aluminum silicate, though 100% could be used. The presence of this filler renders the restored material the property of sufficient radio-opacity, to contrast with tooth tissue, provided a minimum of 6.5% barium oxide is present in the composite. The other filler could be lithium aluminum silicate. The particle size distribution of these fillers varies from less than 5 to approximately 40 microns. These fillers have to be silanated in order to increase the bonding between the inorganic filler and the organic matrix material. The silane bonding agents have a general formula $RSiX_3$, R_2SiX_2 and R_3SiX , where X may be halogen, alkoxy or hydroxy group and R may be vinyl, methacrylate, allyl, methallyl itaconate, maleate, acrylate, itaconate, maleate acrylate aconitrate, fumarate, alkyl, aryl, alkenyl crotonate, cinnamate and citraconate, sorbate or glycidyl groups. When silanation is complete a mono molecular coating of the bonding agent is present on the filler surface, which improves the adhesion between the filler and the resin matrix. Many other suitable fillers such as quartz and alumina could also be used.

The dental restorative material of this invention is polymerized by exposing it to an activator, an energy source which activates a photoreaction. The source of this actinic radiation in this invention is an ultraviolet diagnostic lamp manufactured by Blank Light Eastern a division of Spectronics

Corp. of Westbury, Long Island, New York and designated as Spectroline B-100. The Spectroline B-100 is a high pressure mercury vapor lamp of 100 watts having a radiation wavelength capacity of 3200A⁰ to 4200A⁰ units. The spot bulb used in this lamp is cooled by a fan. An average amount of material for filling i.e., 0.2 to 0.3 gm of the material polymerized completely by irradiation with the above lamp for 20-30 seconds when the material was kept 4 inches away from the lamp. Under these conditions, the material polymerized up to a depth of about 2 millimeters.

10 Examples are carried out with various ingredients in the following range:

	<u>Parts by weight</u>
Resin (including inhibitor)	10-25
Diluent monomer (including inhibitor)	2-5
Alpha diketone or its derivative	.001-1
Amine	.01-2
Filler	70-85

The composite material is made as follows:

20 The resin is mixed with the diluent monomer, photo initiator and the accelerator. These are mixed well in a glass vessel by means of a Teflon (Regd. TM of duPont) rod. When the mix is fairly uniform, barium aluminum silicate is added and mixed well. Finally, the rest of the filler is added in three or four installments and mixed well and allowed to be stored for one week before testing. The well mixed heavy paste is packed in a split cylindrical polytetrafluoroethylene mold, 12.5 mm high by 6mm diameter and open at both ends. The top and bottom were covered with Mylar (Reg. TM of DuPont Co) strips and pressed to get a smooth surface. The Mylar covered ends

30 were exposed for 15 seconds each to the light emitted from

Spectroline B-100 high pressure mercury lamp at a distance of 4 inches. The split mold was then opened and each side of the specimen exposed to actinic radiation for 15 seconds. The total exposure time is one minute. After 10 minutes aging, the polymerized composite was tested and found to have a strength varying from 2700 to 33000 psi. The strength increases to 40,000 if the cured sample is aged for two weeks. On prolonged aging the strength reaches up to 45000 psi.

EXAMPLE 1

10

	<u>Percent by weight</u>
Bis-GMA resin (including MEHQ 200 ppm)	18
Methyl Methacrylate (including MEHQ 100 ppm)	3
4,4'-oxydibenzil	0.2
Trihexylamine	0.2
Barium aluminum silicate	23
Lithium aluminum silicate	55.6

This composite was prepared by the method described previously and the strength of polymerized material on exposure to Spectroline B-100 lamp determined. Upon half minute exposure, the material becomes 25,000 psi strong; one minute exposure 30,000 psi and 5 minutes exposure 36,700 psi.

EXAMPLE II

20

	<u>Percent by weight</u>
Bis-GMA resin (including MEHQ 200 ppm)	18
1,3-butylene dimethacrylate MEHQ 50 ppm	3
4,4'-dimethoxybenzil	0.08
N-methyldibutylamine	0.2
Barium aluminum silicate	23
Lithium aluminum silicate	55.72

The strength of this composite was measured as before. On exposure to Spectroline B-100 lamp for 1 minute it is found to be 30,000 psi.

EXAMPLE III

	<u>Parts by Weight</u>
Bis-GMA resin (including MEHQ 200 ppm)	18
Triethyleneglycoldimethacrylate (including MEHQ 100 ppm)	3
Benzil	0.08
N-methyldibutylamine	0.2
Barium aluminum silicate	23
Lithium aluminum silicate	55.72

The strength of the polymerized material when exposed to Spectroline B-100 lamp for a total period of 1 minute is 29500 psi.

EXAMPLE IV

10 In Example III, the diluent monomer is replaced with the same amount of 2-ethylhexylacrylate. The measured strength of one minute exposure to Spectroline B-100 lamp, is 32,000 psi. Generally the acrylate monomers are more reactive than methacrylate and dimethacrylate monomers.

EXAMPLE V

Bis-GMA resin (including MEHQ 200 ppm)	18
Methylmethacrylate (including MEHQ 100 ppm)	3
Benzophenone	0.4
Triethylamine	0.4
Barium Aluminum silicate	23
Lithium aluminum silicate	55.2

20 No cure was noticed where this mix is exposed to Spectroline B-100 lamp for 4 minutes.

EXAMPLE VI

Example V was repeated with benzil instead of benzophenone. As usual the composite was packed in half inch mold and exposed to Spectroline B-100 lamp for a total period of 1 minute. The strength of the polymerized material is 33,000 psi.

EXAMPLE VII

Example V was repeated with diphenyl triketone $C_6H_5COCOCOC_6H_5$ instead of benzophenone. After exposure to Spectroline B-100 lamp, for a period of one minute, the strength

is only 7400 psi.

EXAMPLE VIII

	<u>Percent by Weight</u>
Bis-GMA resin (including MEHQ 200 ppm)	18
Methylmethacrylate (including MEHQ 100 ppm)	3
4,4'-oxydibenzil	.05
Tetraethylethylenediamine	.09
Barium aluminum silicate	23
Lithium aluminum silicate	55.86

In this example a diamine is used. The strength of the polymerized material on exposure to Spectroline for a total of 1 minute is 30,000 psi.

EXAMPLE IX

10

	<u>Percent by Weight</u>
Bis-GMA resin (including MEHQ 200 ppm)	18
Methylmethacrylate (including MEHQ 100 ppm)	3
4,4'-oxydibenzil	0.2
Diisopropylamine	0.2
Barium aluminum silicate	23
Lithium aluminum silicate	55.6

In this case a secondary amine is used. After mixing the composite is packed in 12.5 mm x 6 mm Teflon mold as described before. The mylar covered ends are exposed for 15 seconds each to Spectroline B-100 lamp. When the mold was opened, the specimen was broken in the middle indicating the reaction is slow. Therefore the mylar covered ends are exposed to 30 seconds each and after opening the mold without damaging the size and shape of the specimen, each side was exposed another 30 seconds each. Thus the total exposure time is 2 minutes. The crush strength under these conditions was found to be 26,000 psi.

20

EXAMPLE X

Example IX was repeated with a primary amine, n butylamine. The strength on two minutes exposure to Spectroline B-100 lamp is 16,000 psi. Thus, it is found the tertiary amine is the most suitable amine.

B

EXAMPLE XI

In this example, a different form of resin is used. Glycidyl ether of Bisphenol-A is reacted with glacial acrylic acid and the reacted product, bisphenol-A-bis(3-acrylato-2-hydroxypropyl) ether is used to prepare the composite.

	<u>Percent by Weight</u>
Bisphenol-A-bis(3-acrylato-2-hydroxypropyl ether (including MEHQ 100 ppm)	18
1,6-hexanedioldiacrylate (including HQ 200 ppm)	3
Benzil	.08
Trihexylamine	.2
Barium aluminum silicate	23
Lithium aluminum silicate	55.72

This composite was treated the same was as before. On exposure to Spectroline B-100 lamp for a total period of one minute gave a material with crushing strength of 31,500 psi.

EXAMPLE XII

	<u>Percent by Weight</u>
Bis-GMA resin (including MEHQ 200 ppm)	23.9
1,6-hexanedioldiacrylate (includ. 200 ppm)	3.9
Benzil	0.1
Trihexylamine	0.26
Silica	72.34

The crush strength of this composite on exposure to Spectroline B-100 for a total period of 1 minute is 27,000 psi.

The best suitable formulation for dental filling material is given below:

	<u>Percent by Weight</u>
Bis-GMA resin (including MEHQ 200 ppm)	18
1,6-hexanedioldiacrylate (including MEHQ 100 ppm)	2.8
Benzil	.08
Trihexylamine	.2
Barium aluminum silicate	23
Lithium aluminum silicate	55.82

Five pounds of the above mix was made using a mechanical stirrer and tested the same way as before. The polymerized material was

found to have 32,000 psi on exposure to Spectroline B-100 lamp for a total period of 1 minute.

The composite made according to the best mode was aged in dark for more than three years at room temperature and tested again. It duplicated the curing and strength characteristics of the fresh material. This confirmed the long shelf life of the product.

10 Since the dentists can use the composite without any addition or mixing restorations essentially free of occluded air bubbles are possible. This eliminates a great deal of mechanical defects and improves the finishing of the restoration to give a smoother solid surface. A smooth surface is less prone to staining as well as bacterial accumulation and gives a smooth feel to the tongue.

20 Radiation of wavelengths between 2970 and 3200A⁰ is capable of inducing cutaneous sunburn and carcinogenesis. This narrow band is responsible for "photo toxic reactions". The polymerization reaction was repeated after filtering the radiation completely up to 3200A⁰. No change in strength of the polymer was observed.

By interposing different optic filters between the lamp and the material, it is found that the most effective polymerization occurred with lights between 4000A⁰-4500A⁰ i.e. the visible region.

30 The cure test was repeated with a tungsten-halogen lamp, a source of visible light, manufactured by General Electric Co. The light was focused to the material through a half foot long fibre bundle. It is found that the material cured more effectively with tungsten-halogen lamp than with mercury lamp.

In addition to the composite restorative material, the present invention leads to the preparation of one phase (as opposed to two phase systems known in the prior art) pit and fissure sealants, bonding agents, cavity liners, and restoration glazes which collectively are referred to as coating compositions. All these compositions contain essentially a photo polymerizable aromatic resin such as Bis-GMA, a diluent monomer such as methacrylate, dimethacrylate, acrylate or diacrylate, a photo initiator and an accelerator. These dental compositions differ from the above-mentioned restorative materials, in that they do not contain any fillers or have reduced filler levels. These compositions polymerize in the oral environment by the application of actinic radiation.

The pit and fissure sealant, cavity liner, glaze material or bonding agent contain generally 70 to 80% by weight of Bis-GMA resin, 30% to 20% methylmethacrylate inhibited with 100 ppm MEHQ, 0.01 to 1% photo initiator and 0.01 to 1% accelerator. The best formulation is -

Bis-GMA resin (inhibited with 200 ppm MEHQ)	75 parts
Methylmethacrylate (inhibited with 100 ppm MEHQ)	25 parts
Benzil	0.5 parts
Trihexylamine	0.5 parts

This unfilled mix can be used as pit and fissure sealant, bonding agent, cavity liner and restorative glaze material. Even though any other methacrylate, acrylate, dimethacrylate, dicrylate or triacrylate could be used as a diluent monomer for the above preparation, the one with methylmethacrylate has the best property as a thin film. The amount of methylmethacrylate could be varied to adjust the viscosity of the mix. This single component sealant

system has one year shelf life in air tight and light resistant bottles.

10 Though the best modes are described herein, the variations in the formulae are possible. An increase in the quantity of diluent reduces the viscosity. An increase in the filler quantity increases the strength but thickens the paste. Strength is also increased, with the increase in the quantity of benzil. Too much benzil should be avoided since it imparts a yellow color and may cause polymerization if the material is exposed to incident light. The initiator and accelerator combination composition described can be used to photopolymerize a variety of monomer resins.

 Thus, the dental material gives an option to the dentists to use sufficiently powerful visible light to polymerize the material to avoid the potential risk involved in using ultraviolet light. (Journal of American Dental Association, Vol. 92, April 1976).

20 Although specific components proportions and procedures have been stated in the above descriptions of the preferred embodiments of the novel dental filling composition, other suitable materials and procedures such as those described above may be employed to synergize, enhance or otherwise modify the novel method. Other modifications and ramifications of the present invention would appear to those skilled in the art upon a reading of this disclosure. These are intended to be included within the scope of this invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A one phase photopolymerizable composite dental restorative composition comprising:

(a) a monomer resin which is an adduct of diglycidyl ether of bisphenol A and methacrylic acid or acrylic acid;

(b) a diluent monomer;

(c) an alpha diketone of the formula



where R and R' can be same or different aliphatic or aromatic groups and their derivatives;

(d) an amine and

(e) fillers.

2. The composition of claim 1 where the diluent monomer is a mono, di or tri functional acrylate or methacrylate.

3. The composition of claim 2 where the diluent is 1,6 hexanedioldiacrylate.

4. The composition of claim 1 wherein the alpha diketone is benzil.

5. The composition of claim 6 wherein the amine is a tertiary amine.

6. The composition of claim 5 wherein the tertiary amine is trihexylamine.

7. The composition of claim 1 wherein the filler is x-ray opaque.

C

8. The composition of claim 7 wherein the x-ray opaque filler is barium aluminum silicate.

9. The composition of claim 1 wherein the filler is lithium aluminum silicate.

10. The composition of claim 1 wherein the filler is a mixture of barium aluminum silicate and lithium aluminum silicate.

11. The composition of claim 1 wherein the ingredients comprise the following proportions by weight:

Monomer resin	10-25
Diluent monomer	2-5
Diketone (initiator)	.001-1
Amine (accelerator)	.01-2
Barium aluminum silicate (filler)	0-85
Lithium aluminum silicate (filler)	0-85

12. The composition of claim 1 wherein the ingredients comprise the following proportions by weight:

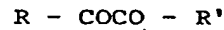
Monomer including resin MEHQ 200 ppm	18
1,6-hexanedioldiacrylate including MEHQ 100 ppm (diluent monomer)	28
Benzil (initiator)	0.08
Trihexylamine (accelerator)	0.2
Barium aluminum silicate (filler)	23
Lithium aluminum silicate (filler)	55.82

13. A one phase photopolymerizable composite dental restorative composition comprising:

(a) a monomer resin which is an adduct of diglycidyl ether of bisphenol A and methacrylic acid or acrylic acid;

(b) a diluent monomer;

(c) an alpha diketone of the formula



where R and R' can be same or different aliphatic or aromatic groups and their derivatives; and

(d) an amine.

14. The coating composition of claim 15 wherein the diluent monomer is methylmethacrylate.

15. The coating composition of claim 13 wherein the alpha diketone is benzil.

16. The coating composition of claim 20 wherein the amine is a tertiary amine.

17. The coating composition of claim 16 wherein the tertiary amine is trihexylamine.

18. The composition of claim 13 wherein the ingredients comprise the following range by weight:

monomer resin	70-80 parts
diluent monomer	20-30 parts
diketone	0.01-1 parts
amine	0.01-1 parts

19. The composition of claim 13 wherein the ingredients are:

Monomer resin	75 parts
Methylmethacrylate	25 parts
Benzil	0.5 parts
Trihexylamine	0.5 parts

20. The composition of claim 1 or claim 13 further polymerized by radiation of wavelength between the range of 3600\AA to 4500\AA .

